

CHAPTER 3

CRYSTALS

Crystalline and noncrystalline materials

Matter exists in three states namely solids, liquids and gases. As the atoms or molecules in solids are attached to one another with strong forces of attraction, the solids have definite volume and shape. In this chapter we shall deal with physical properties of crystals.

Single crystals and polycrystals

Single crystals

The crystalline state of a solid is characterised by regular or periodic arrangement of atoms or molecules. The crystalline solids may be subdivided into single crystals and polycrystals. In single crystals the periodicity of atoms extends throughout the material. Diamond, quartz, mica, silicon etc. are examples of single crystals. Single crystals exist in nature, but they also be produced artificially. They are ordinary difficult to grow, because the environment must be carefully controlled.

If the extremities of a single crystal are permitted to grow without any external constraint, the crystal will assume a regular geometric shape having flat faces as with some of the gemstones; the shape is indicative of the crystal structure. Within the past few years, single crystals have become extremely important in many of our modern technologies, in particular electronic microcircuits which employ single crystals of silicon and other semiconductors.

Polycrystals

A polycrystalline is an aggregate of a number of small crystallites with random orientations separated by well defined boundaries. Metals and ceramics are polycrystals. There are various

stages in the solidification of a polycrystalline specimen. Initially small crystals or nuclei form at various positions. These have random crystallographic orientations as indicated by the square grid in figure 3.1. The small grains grow by the successive addition from the surrounding liquid of atoms to the structure of each. The extremities of adjacent grains impinge on one another as the solidification process approaches completion. The crystallographic orientation varies from grain to grain. Also there exists some atomic mismatch. Within the region where two grains meet; this area is called a grain boundary.

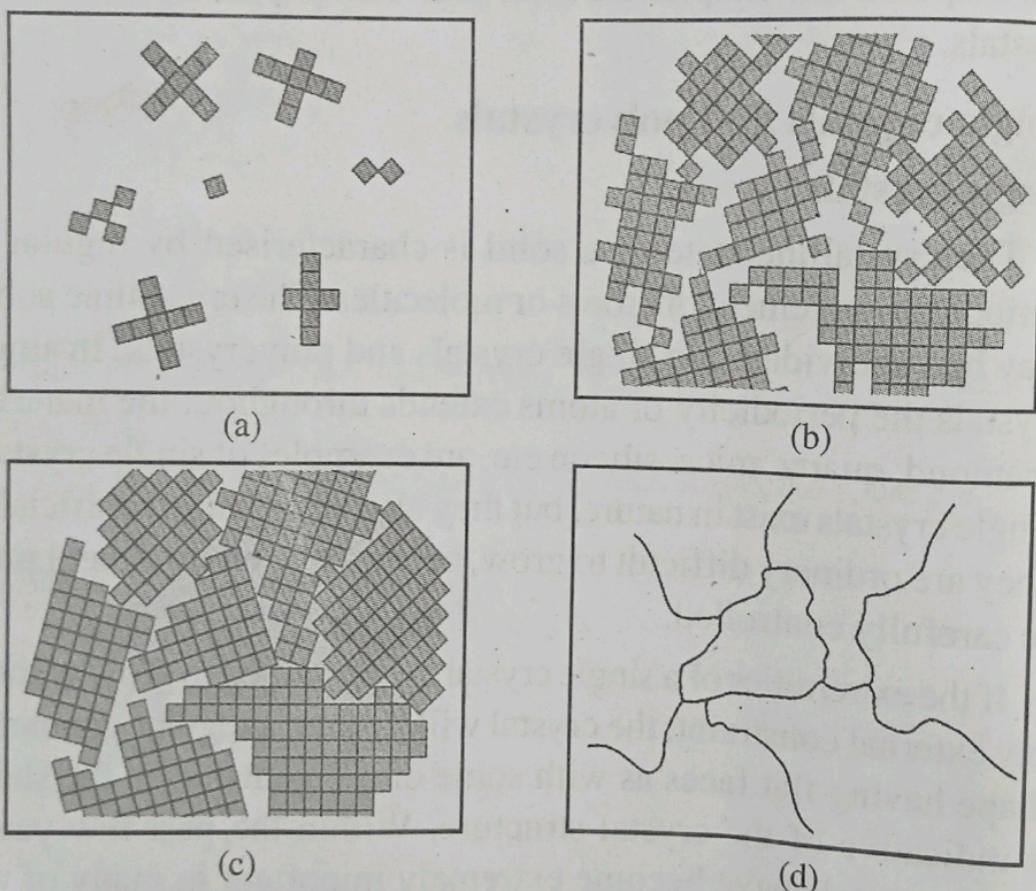


Figure 3.1: Schematic diagrams of the various stages in the solidification of a polycrystalline material; the square grids depict unit cells

- (a) Small crystallite nuclei (b) Growth of the crystallites; the obstruction of some grains that are adjacent to one another is also shown. (c) Upon completion of solidification, grains having irregular shapes have formed (d) The grain structure as it would appear under the microscope; dark lines are the grain boundaries.

Anisotropy

Substances which exhibit same physical properties in all directions are said to be isotropic. In other words the physical properties are independent of the crystallographic direction along which physical properties are measured. Glass, NaCl, metals etc are isotropic. However the physical properties of single crystals of some substances depend on the crystallographic direction in which measurements are taken. This directionality of properties is called anisotropy. For example the elastic modulus, the electrical conductivity and the refractive index may have different values in different directions of crystals. Single crystalline diamond, quartz, wood, composite materials are examples of anisotropic materials.

The directionality of properties is associated with the symmetry of the crystal structure. The degree of anisotropy increases with decreasing structural symmetry.

It may be noted that a crystal can be isotropic or anisotropic for a certain property and the same crystal can be isotropic for one property but anisotropic for another property. Cubic crystals are good examples. Any cubic crystal is necessarily isotropic for electrical conductivity but not for young's modulus.

In the case of polycrystalline materials the crystallographic orientations of the individual grains are totally random. Even though each grain may be anisotropic, a substance composed of the grain aggregate behaves isotropically. Also the magnitude of a measured property represents some average of the directional values. Sometimes the grains in polycrystalline materials have a preferential crystallographic orientation then the material is said to have a texture.

Noncrystalline solids (Amorphous)

These are solids characterised by the random arrangement of atoms or molecules. The periodicity, if at all present, extends upto a distance of a few atomic diameters only. In other words; these

solids exhibit short range order. Glass, plastics, rubbers, cements, paraffin wax etc. are non crystalline solids (amorphous).

The ceramic compound silicon dioxide may exist in crystalline and non crystalline states. See figure 3.2. Whether a crystalline or amorphous solid forms depends on the ease with which a random atomic structure in the liquid can transform to an ordered state during solidification. For example rapidly cooling liquid through the freezing temperatures favours the formation of a non crystalline solid, since only little time is allowed for the ordering process.

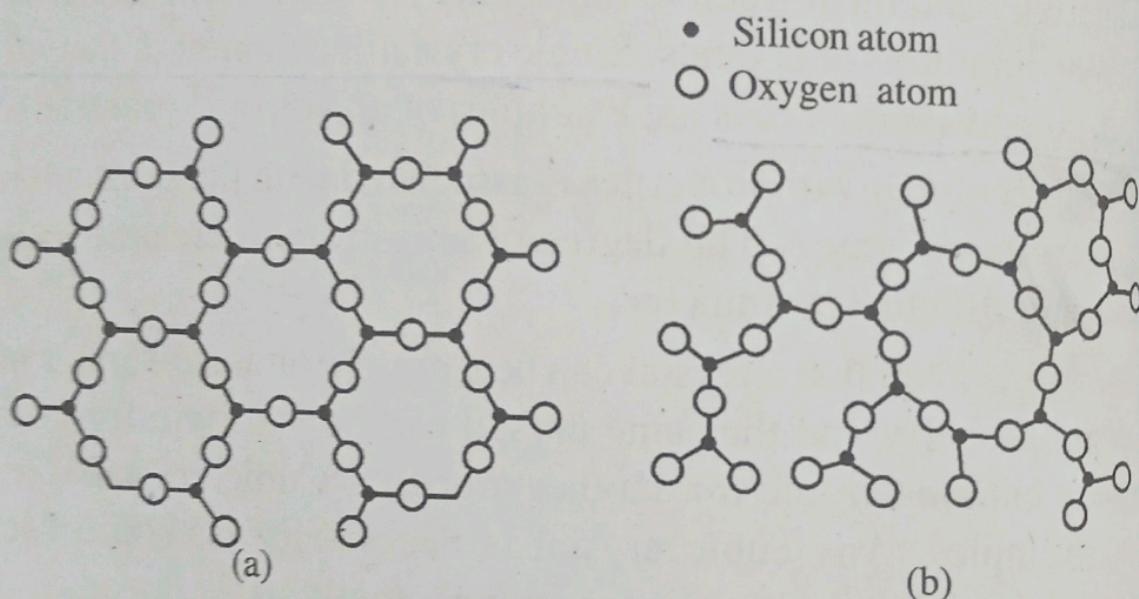


Figure 3.2: Two dimensional schemes of the structure of (a) crystalline silicon dioxide and (b) noncrystalline silicon dioxide

Metallic crystal structures

The atomic bonding in this group of materials is metallic and thus non directional in nature, this leads to relatively large number of nearest neighbours and dense atomic packings for most metallic crystal structures.

Most of the common metals exhibit simple crystal structures such as cubic, face centred cubic and hexagonal close packed. Here our aim is to see how atoms are packed in these crystal structures. For this we have to familiar with certain crystal structure terms such as coordination number, number of second nearest neighbour

nearest neighbour distance, atomic radius number of atoms per unit cell and atomic packing factor.

Coordination number or number of nearest neighbours (N)

It is defined as the number of equidistant neighbour that an atom has in the given structure. It is denoted by N.

Greater the coordination number, the more closely packed up will be the structure.

For SC structure, $N = 6$

For BCC structure, $N = 8$

For FCC structure, $N = 12$

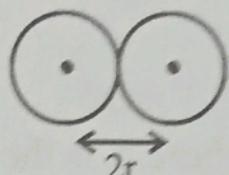


Figure 3.3

Nearest neighbour distance

The distance between the centres of two nearest neighbouring atoms is called nearest neighbour distance. If r is the radius of the atom, the nearest neighbour distance is $2r$.

For SC structure, $2r = a$

For BCC structure, $2r = \frac{\sqrt{3}}{2}a$

For FCC structure, $2r = \frac{a}{\sqrt{2}}$

Number of second nearest neighbours

It is the number of equidistant atoms nearest to first nearest number.

There are 12 second nearest neighbours at distance $\sqrt{2}a$ for SC. There are 6 second nearest neighbours at distance a in BCC. There are 6 second nearest neighbours at distance a in FCC structures.

Atomic radius (r)

It is defined as half the distance between nearest neighbours in a crystal without impurity.

For SC, $r = \frac{a}{2}$, for BCC, $r = \frac{\sqrt{3}}{4}a$ and for FCC, $r = \frac{a}{2\sqrt{2}}$

Number of atoms per unit cell

The number of effective lattice points (atoms) per unit cell given by

$$n_{\text{eff}} = n_i + \frac{n_f}{2} + \frac{n_e}{8}$$

where n_i is the number of lattice points (atoms) completely inside the cell and n_f and n_e represent the lattice points occupying face centre and corner positions of the cell respectively.

For SC structure:

$$n_i = 0, n_f = 0 \text{ and } n_e = 8$$

$$\therefore n_{\text{eff}} = 1 \times 0 + \frac{1}{2} \times 0 + \frac{1}{8} \times 8 = 1$$

For BCC structure:

$$n_i = 1, n_f = 0 \text{ and } n_e = 8$$

$$\therefore n_{\text{eff}} = 1 \times 1 + \frac{1}{2} \times 0 + \frac{1}{8} \times 8 = 2$$

For FCC structure:

$$n_i = 0, n_f = 6 \text{ and } n_e = 8$$

$$\therefore n_{\text{eff}} = 1 \times 0 + \frac{1}{2} \times 6 + \frac{1}{8} \times 8 = 4$$

Atomic packing fraction (APF)

The packing of atoms in a unit cell of the crystal structure of material is represented by atomic packing fraction (APF).

It is defined as the ratio of volume occupied by the atoms in a unit cell to that of the unit cell.

$$\text{i.e., } \text{APF} = \frac{\text{Volume of the atoms per unit cell}}{\text{Volume of the unit cell}}$$

$$= \frac{n_{\text{eff}} \times \text{Volume of each atom}}{\text{Volume of the unit cell}}$$

$$\text{APF} = \frac{V}{V}$$

Packing factor of simple cubic crystal structure

The simple cubic crystal structure of unit cell consists of atoms located at the corners only (each atom at each corner) and these atoms touch each other along the cube edges. Thus in sc structures we have

$$\text{lattice constant, } a = 2r$$

In sc each atom is surrounded by six equidistant nearest neighbours and hence the coordination number is 6.

Moreover each corner atom is shared by eight unit cells. Hence the share of each corner atom to a unit cell is one-eighth of an atom.

$$\therefore \text{The total number of atoms in effect in one unit cell} = \frac{1}{8} \times 8 = 1$$

In other words the effective number of lattice points in a simple cubic cell is one. Thus sc is a primitive cell.

$$\therefore \text{Volume of all the atoms in a unit cell } V = 1 \times \frac{4}{3} \pi r^3$$

$$\text{Volume of the unit cell, } V = a^3 = (2r)^3$$

$$\therefore \text{The packing factor, } P.F = \frac{V}{V} = \frac{4\pi r^3}{3(2r)^3}$$

i.e., $P \cdot F = \frac{\pi}{6} = 0.52$ or 52%.

Since only half the space of unit cell is filled with atoms we can say that sc structure is loosely packed structure.

Only one element polonium at a certain temperature exhibits this structure.

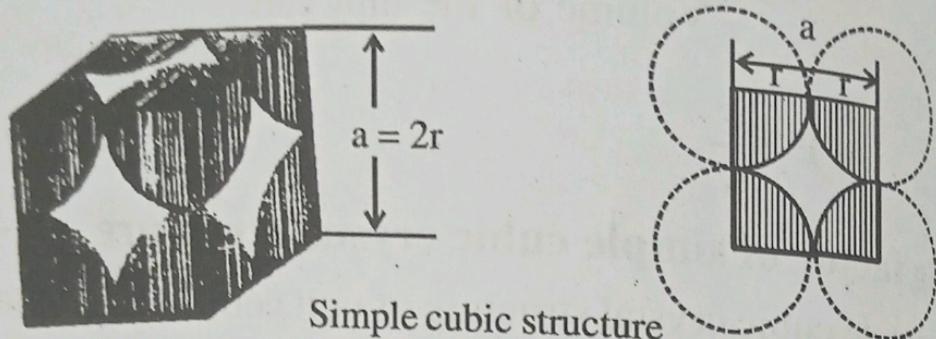


Figure 3.4

Packing factor of body centred cubic structure

In this structure of unit cell there are 8 atoms at the corners and one another atom at the body centre. The atoms at the corners do not touch each other but the corner atom touches the body central atom along the body diagonal. Hence the coordination number is 8.

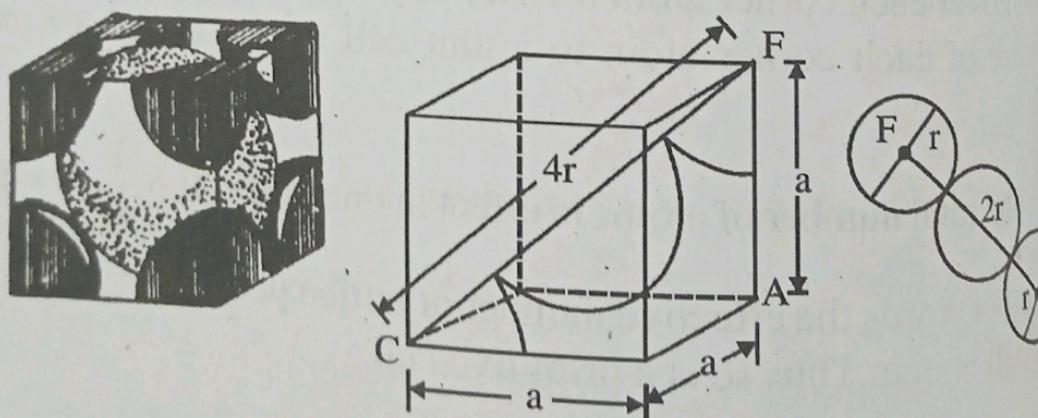


Figure 3.5 : Body centred cubic structure

The number of atoms in the unit cell $= 8 \times \frac{1}{8} + 1 = 2$

Volume of the atoms in the unit cell $V = 2 \times \frac{4}{3} \pi r^3$

Volume of the unit cell, $V = a^3$

$$\therefore \text{Packing factor, } P \cdot F = \frac{V}{V} = \frac{8\pi r^3}{3a^3} \quad \dots \dots (1)$$

From the figure, we have

$$(AC)^2 = a^2 + a^2 = 2a^2$$

$$(FC)^2 = (AC)^2 + (AF)^2$$

$$(FC)^2 = 2a^2 + a^2 = 3a^2$$

$$(4r)^2 = 3a^2$$

$$r = \frac{\sqrt{3}}{4} a$$

Put this in eqn (1), we get

$$P \cdot F = \frac{8\pi}{3} \frac{\left(\frac{\sqrt{3}}{4} a\right)^3}{a^3} = \frac{\sqrt{3}\pi}{8} = 0.68 = 68\%.$$

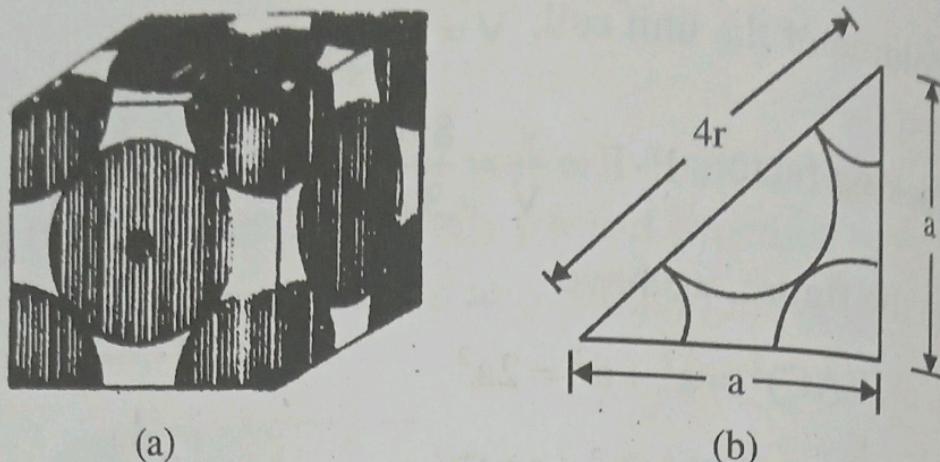
Li, Na, K and Cr exhibit this structure.

Packing factor of face centred cubic structure

In this structure there are eight atoms at eight corners of the unit cell and six atoms at the centres of six faces. The atoms touch each other along the face diagonal. Each corner atom is shared by 8 surrounding unit cells and each of face centred atom is shared by 2 surrounding unit cells.

\therefore The total number of atoms in the unit cell

$$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

**Figure 3.6: Face centred cubic structure**

Volume of all atoms in the unit cell, $V = 4 \times \frac{4}{3} \pi r^3$

Volume of the unit cell, $V = a^3$

\therefore The packing factor, $P.F = \frac{V}{V}$

$$\text{i.e., } P.F = \frac{16\pi r^3}{3 \times a^3}$$

From the figure we have

$$(4r)^2 = a^2 + a^2 = 2a^2$$

$$\text{or } r = \frac{a}{2\sqrt{2}}$$

Put this in eqn (1), we get

$$P.F = \frac{16\pi \times a^3}{3a^3(2\sqrt{2})^3} = \frac{\pi}{3\sqrt{2}} = 0.74$$

Copper, aluminium, lead and silver exhibit this structure. It is a close packed structure.

Note: The coordination number of each atom in fcc is 12. When the coordination number of an atom is less than 12, we call it as a loose packed structure.

Packing factor of hexagonal close packed structures (hcp)

The very name hexagonal indicates that hcp structure has the shape of hexagon. The unit cell of this contains one atom at each corner, one atom each at the centre of the hexagonal faces and three more atoms within the body of the cell. The atoms touch each other along the edge of the hexagon. Thus $a = 2r$.

The top layer of the hexagon contains seven atoms. Each corner atom is shared by 6 surrounding hexagonal cells and the centre atom is shared by 2 surrounding cells. The three atoms within the body of the cell are fully contributing to the cell.

Thus the total number of atoms in the unit cell

$$= 6 \times \frac{1}{6} + 6 \times \frac{1}{6} + 1 \times \frac{1}{2} + 1 + \frac{1}{2} + 3 = 6$$

\therefore Volume of atoms in the unit cell, $v = 6 \times \frac{4}{3} \pi r^3$

$$v = \frac{24}{3} \pi \left(\frac{a}{2}\right)^3 = \pi a^3$$

Volume of the unit cell (hexagon), $V = \frac{3\sqrt{3}}{2} a^2 c$

(where c be the height of the unit cell and a be its edge).

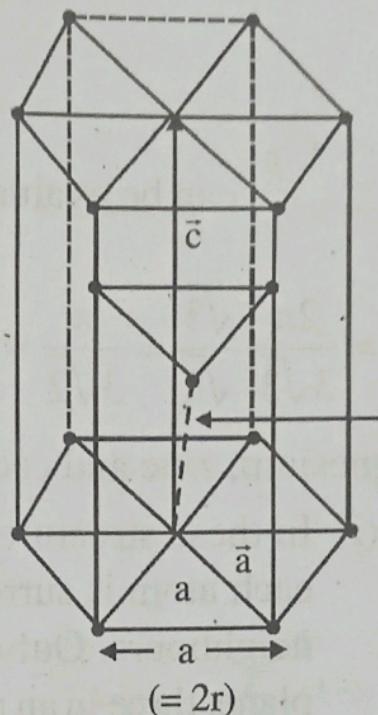


Figure 3.7: Hexagonal close packed structure

$$\therefore \text{Packing factor, } PF = \frac{V}{V} = \frac{\pi a^3}{\frac{3\sqrt{3}}{2} a^2 c} = \frac{2\pi}{3\sqrt{3}} \left(\frac{a}{c} \right)$$

$\frac{a}{c}$ can be evaluated to be $\sqrt{\frac{3}{8}}$

$$\therefore P.F = \frac{2\pi}{3\sqrt{3}} \frac{\sqrt{3}}{\sqrt{8}} = \frac{\pi}{3\sqrt{2}} = 0.74 \text{ or } 74\%.$$

Magnesium, zinc and cadmium exhibit this structure.

- Note :** (i) In these structures the coordination number is 12, i.e., each atom is surrounded by 12 similar and equal sized neighbours. Out of these 12 neighbours, six lie in one plane, three in an adjacent parallel plane above this plane and three in a similar plane below it.
- (ii) Volume of the hexagon = base area \times height = base area \times c

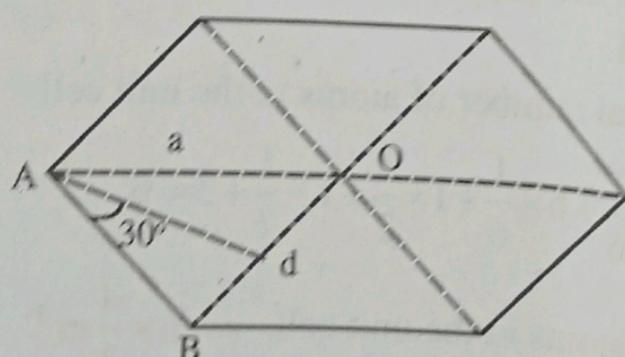


Figure 3.8

Base area = 6 \times Area of $\triangle AOB$.

$$= 6 \times \frac{1}{2} AO \times Bd$$

$$\text{But } \frac{Ad}{AB} = \cos 30^\circ \therefore Ad = AB \cos 30^\circ = a \frac{\sqrt{3}}{2}$$

$$\text{Base area} = 6 \times \frac{1}{2} \times a \times a \frac{\sqrt{3}}{2} = \frac{3\sqrt{3}}{2} a^2$$

$$\therefore \text{Volume of the hexagon} = \frac{3\sqrt{3}}{2} a^2 c.$$

To evaluate $\frac{a}{c}$

The three body atoms lie in

a horizontal plane at $\frac{c}{2}$ from
the orthocentres of alternate
equilateral triangles.

From the figure

$$AZ^2 = AX^2 + ZX^2$$

$$a^2 = \left(\frac{2}{3} \times \text{median} \right)^2 + \frac{c^2}{4}$$

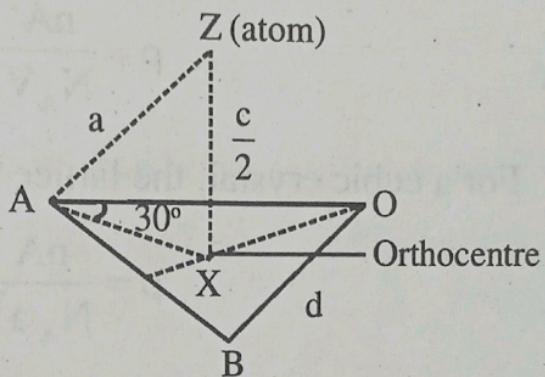


Figure 3.9

$$a^2 = \frac{a^2}{3} + \frac{c^2}{4}, \quad a^2 - \frac{a^2}{3} = \frac{c^2}{4}$$

$$\frac{2}{3}a^2 = \frac{c^2}{4}, \quad \frac{a^2}{c^2} = \frac{3}{8}$$

$$\therefore \frac{a}{c} = \sqrt{\frac{3}{8}}$$

Density computations

Consider a crystal of lattice constant a having unit cell volume V . Let ρ be the density of the crystal.

If A is the atomic weight of the material and N_A the avagadro number. Thus $\frac{A}{\rho}$ of the material will contain N_A atoms. Hence,

atoms in the unit cell occupy a volume $\frac{A_n}{\rho N_A}$. This is equal to V.

i.e.,

$$V = \frac{A_n}{\rho N_A}$$

or

$$\rho = \frac{nA}{N_A V} \quad \dots\dots (2)$$

For a cubic crystal, the lattice is a, thus $V = a^3$

$$\rho = \frac{nA}{N_A a^3}$$

or

$$a = \left(\frac{nA}{N_A \rho} \right)^{1/3} \quad \dots\dots (3)$$

Example 1

Copper has fcc structure and its atomic radius is 0.128nm. Calculate its density. Take the atomic weight of copper as 63.5 g/mol.

Solution

The number of atoms per unit cell for fcc structure,

$$n = 4.$$

Volume of the unit cell,

$$V = a^3$$

where $a = 2\sqrt{2} r$

$$V = (2\sqrt{2} r)^3 = 16\sqrt{2} r^3.$$

We have

$$\rho = \frac{nA}{VN_A} = \frac{4 \times 63.5}{16\sqrt{2r^3 \times 6.023 \times 10^{23}}}$$

$$r = 0.128 \times 10^{-9} \text{ m given}$$

$$r = 1.28 \times 10^{-8} \text{ cm}$$

$$\rho = \frac{4 \times 63.5}{16\sqrt{2}(1.28 \times 10^{-8})^3 \times 6.023 \times 10^{23}}$$

$$\rho = 8.89 \text{ gcm}^{-3}.$$

Example 2

Calculate the lattice constant for α -iron belonging to bcc structure. Take the density of α -iron as $7.86 \times 10^3 \text{ kgm}^{-3}$ and the atomic weight of iron as 55.85.

Solution

For bcc structure, the volume of the unit cell,

$$\text{and } V = a^3$$

$$n = 2$$

$$\rho = 7.86 \times 10^3 \text{ kgm}^{-3}$$

$$A = 55.85 \times 10^{-3} \text{ kg/mol}$$

Using

$$a = \left(\frac{nA}{N_A \rho} \right)^{1/3}$$

$$a = \left(\frac{2 \times 55.85 \times 10^{-3}}{6.02 \times 10^{23} \times 7.86 \times 10^3} \right)^{1/3}$$

$$a = 0.124 \text{ nm.}$$

Example 3

Zinc has hcp structure. The height of the unit cell is 0.494. The nearest neighbour distance is 0.21. The atomic weight of zinc is 65.37. Calculate the volume of the unit cell and density of zinc.

Solution

$$a = 0.27 \times 10^{-9} \text{ m}$$

$$c = 0.494 \times 10^{-9} \text{ m}$$

Volume of the unit cell

$$V = \frac{3 \times \sqrt{3} \times (0.27 \times 10^{-9})^2 \times (0.494 \times 10^{-9})}{2}$$

$$V = 9.356 \times 10^{-29} \text{ m}^3.$$

The number of atoms belonging to a unit cell of hcp, $n = 6$.

Using

$$\rho = \frac{nA}{N_A V}$$

$$\rho = \frac{6 \times 65.37 \times 10^{-3}}{6.02 \times 10^{23} \times (9.356 \times 10^{-29})}$$

$$\rho = 6964 \text{ kgm}^{-3}.$$

Linear and planar densities

The linear density of a crystal is related to directional equivalency. This means that equivalent directions have identical linear densities. The corresponding parameter for crystallographic planes is planar density.

Linear density (LD)

It is defined as the number of atoms per unit length whose centres lie on the direction vector for a specific crystallographic direction.

$$LD = \frac{\text{Number of atoms centred on the direction vector}}{\text{length of direction vector}}$$

The unit of LD is m^{-1} . For example the linear density of [110] direction for the fcc crystal,

$$LD_{110} = \frac{2 \text{ atoms}}{4R} = \frac{1}{2R}$$

Planar density

It is defined as the number of atoms per unit area that are centred on a particular crystallographic plane.

$$PD = \frac{\text{Number of atoms centred on a plane}}{\text{Area of plane}}$$

The unit of PD is m^{-2} . For example planar density (110) plane within an fcc unit cell

$$PD_{110} = \frac{2 \text{ atoms}}{8r^2\sqrt{2}}$$

$$= \frac{1}{4\sqrt{2} r^2}$$

\therefore Area of planar region

$$= (4r) 2r\sqrt{2}$$

$$= 8\sqrt{2} r^2$$

Polymorphism and allotropy

Polymorphism

Polymorphism is a common phenomenon of crystalline materials.

It describes the ability of a substance to exist as two or more crystalline phases that have different arrangements of the molecules in the solid state but are otherwise identical in terms of chemical content.

Some common examples of polymorphs are calcite and aragonite. The composition of these two minerals is CaCO_3 , but calcite is rhombohedral while aragonite is orthorhombic. Diamond and graphite, both of which are pure carbon are also polymorphs. Diamond, however is cubic, while graphite is hexagonal.

Iron is also polymorphic. This is one of the secrets to the success of iron to combine with other elements to form alloys to dramatically extend its range as an engineering material.

Allotropy

The property of some metals and alloys that exhibit different crystalline structure at different temperatures and pressures is called allotropy.

Allotropy is a very important property of materials; these allotrophic changes are the basis for heat treatment of many engineering materials.

For example, below 912°C , iron has bcc crystal structure and is called α -iron. But above 912°C iron is called γ -iron with fcc crystal structure.

There are two crystalline forms of sulphur in solid states like rhombic sulphur and monoclinic sulphur. These two forms are called allotropes of sulphur. Rhombic sulphur is stable at a temperature lower than 96°C .

UNIVERSITY MODEL QUESTIONS

Section A

(Answer questions in one or two sentences)

Short answer questions

1. What are crystalline solids? Give an example.
2. Distinguish between single and polycrystals.
3. What are amorphous solids? Give an example.
4. What is meant by isotropy of materials?
5. What is meant by anisotropy of materials?
6. What are non crystalline solids? Give two examples.
7. Define
 - a) Coordination number
 - b) Nearest neighbour distance.
8. How do we calculate the number of atoms per unit cell?
9. What is meant by atomic packing factor?
10. Write down an expression for the density of a crystal structure and explain the symbols.
11. Define
 - a) linear density and
 - b) planar density of crystals.
12. What is meant by polymorphism of crystalline materials?
13. What is meant by allotropy of materials?
14. CaCO_3 is a polymorphic material. Explain.
15. Iron is an allotropic material. Explain.

Section B

(Answer questions in a paragraph of about half a page to one page)

Paragraph / Problem type

1. How does a polycrystal is formed?
2. Distinguish between isotropy and anisotropy of materials.

3. A crystal may be isotropic or anisotropic for a certain property. Justify.
4. Distinguish between crystalline and non crystalline solids.
5. Calculate the number of atoms per unit cell for
 - a) SC structure
 - b) BCC structure
 - c) FCC structure.
6. Calculate the atomic packing factor of simple cubic crystal.
7. Show that the atomic packing factor of BCC structure is 68%.
8. Find the packing factor of FCC structure.
9. Find the volume of the hexagonal close packed unit cell.
10. Show that the $\frac{a}{c}$ ratio for an ideal hcp lattice is $\sqrt{\frac{3}{8}}$.
11. Show that the packing factor of hcp structure is 74%.
12. How do we compute the density of crystal structures?
13. Distinguish between linear and planar densities of crystals.
14. Molybdenum has a bcc crystal structure, an atomic radius of 0.1363nm and an atomic weight of 95.94 g/mole. Compute its density. [10.22 gcm⁻³]
15. Calculate the radius of a palladium atom, given that Pd has an fcc crystal structure, a density of 12.0 gcm⁻³ and an atomic weight of 106.4g/mol. [0.138nm]
16. Titanium has an hcp crystal structure and a density of 4.51gcm⁻³. What is the volume of its unit cell? [1.06 × 10⁻²⁸m³]
17. Magnesium has an hcp crystal structure, a $\frac{c}{a}$ ratio of 1.624 and a density of 1.74gcm⁻³. Compute the atomic radius for Mg. [0.160 nm]
18. Cobalt has an hcp crystal structure, an atomic radius of 0.1253nm and a c/a ratio of 1.623. Calculate the volume of the unit cell. [6.64 × 10⁻²(nm)³]

Hints to problems

$$14. \rho = \frac{nA}{N_A V} = \frac{2 \times 95.94}{6.02 \times 10^{23} V}$$

$$r = 0.1363 \times 10^{-7} \text{ cm}$$

$$a = \frac{4r}{\sqrt{3}}$$

$$V = a^3 = \left(\frac{4r}{\sqrt{3}} \right)^3$$

$$15. a = \left(\frac{nA}{N_A \rho} \right)^{1/3} = \left(\frac{4 \times 106.4}{6.02 \times 10^{23} \times 12} \right)^{1/3}$$

$$r = \frac{a}{2\sqrt{2}} \text{ for fcc.}$$

$$16. \rho = \frac{nA}{N_A V}$$

$$V = \frac{nA}{N_A \rho}, n = 6, A = 47.87.$$

$$17. a = \left(\frac{nA}{N_A \rho} \right)^{1/3} \quad n = 6, \rho = 1.74$$

$$r = \frac{a}{2}$$

$$V = \frac{3\sqrt{3}}{2} a^2 c$$

$$\frac{V}{r} = 3\sqrt{3} \frac{c}{a} = 3\sqrt{3} \times 1.624.$$

$$18. \frac{V}{r} = 3\sqrt{3} \frac{c}{a}$$

□